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ALKALINE HYDROLYSIS OF CL-20

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14. ABSTRACT

The Energetics and Warheads Division of the U.S. Army Armament Research, Development and Engineering Center has been involved in the development of CL-20. An alkaline hydrolysis study was performed to better understand the fate and transport of CL-20 through environmental systems.

15. SUBJECT TERMS

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CONTENTS

SUMMARY

CL-20, also known as HNIW (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaaziaisowurtzitane), is a high energy, high density material. Concerns regarding the environmental fate and transport of CL-20 are arising due to its potential introduction into soil and water matrices. The aqueous hydrolysis of CL-20 was investigated as a possible remediation technique. Alkaline hydrolysis experiments were conducted at temperatures of 15, 20, 30, and 40°C, with hydroxide concentrations ranging from 0.25 to 300 mM. Like RDX and HMX, alkaline hydrolysis of CL-20 follows second-order kinetics. CL-20 alkaline hydrolysis was found to proceed at a significantly faster rate than RDX. The temperature dependency of the second-order rate constants was evaluated using the Arrehnius model. The activation energy for CL-20 was found to be within close range of the activation energies reported for RDX and HMX.

INTRODUCTION

The rate of reaction of energetic materials under alkaline conditions depends on the concentrations of the base and the energetic compound. Heilmann et al. (ref. 1) and Hoffsommer et al. (ref. 2) suggested that the alkaline hydrolysis of the nitramines HMX and RDX proceeds via the E-2-elimination mechanism, which is a common elimination mechanism in organic chemistry and follows a second-order rate law. Accordingly, the kinetics of alkaline hydrolysis of CL-20 using a strong base (NaOH) is represented as follows

$$\frac{dC_{CL-20}}{dt} = -k_2 C_{CL-20} C_{NaOH} \tag{1}$$

where C_{CL-20} is the CL-20 concentration, C_{NaOH} is the base concentration, and k_2 is the second-order rate constant. Because the consumption of NaOH cannot be accurately or conveniently measured during the time course of reaction, it is difficult to determine the second-order rate constant (k_2) directly. However, by adjusting the experimental conditions, a pseudo-first order rate constant (k_1) can be obtained. This situation can be realized, by either maintaining the NaOH concentration constant throughout the reaction or at least sufficiently in excess such that any change in the concentration of the base is negligible compared to the change in concentration of CL-20. Under such experimental conditions, equation 1 is reduced to the following pseudo-first order rate equation

$$\frac{dC_{CL-20}}{dt} = -k_1 C_{CL-20} \tag{2}$$

where k_1 is given by

$$k_1 = k_2 C_{NaOH} \tag{3}$$

By monitoring the CL-20 concentration during the time course of the reaction at a given NaOH concentration and temperature, one can obtain k_1 using the integrated form of equation 2

$$\ln C_{CL-20} = \ln C^0_{CL-20} - k_1 t \tag{4}$$

where C^0_{CL-20} is the initial concentration of CL-20. According to equation 4, the slopes of the semi-logarithmic plots of the concentration-time data yield the rate constant k_1. Next, by varying the NaOH concentration at a given temperature, the second-order rate constants can be computed using equation 3.

AQUEOUS HYDROLYSIS SETUP

Batch hydrolysis experiments were carried out at four temperatures (15, 20, 30, and 40°C) below solubility limits (homogeneous alkaline hydrolysis) and above solubility limits (heterogeneous alkaline hydrolysis) using NaOH concentrations ranging from 0.25 to 300 mM. The temperature of the reaction medium was regulated using a water bath (Fisher Scientific, Model Isotemp-210).

Homogeneous Alkaline Hydrolysis Experiments

De-ionized water (495 mL) containing dissolved reactant was placed in a 1-L beaker. A three-blade propeller rotated by an overhead Cole Parmer Stirpak 4554-10 lab stirrer set at 150 rpm was centered and lowered into the beaker and raised to a height of 1 cm above the beaker bottom. Next, 5 mL of concentration NaOH solution of appropriate molarity were added to the solution.

Heterogeneous Alkaline Hydrolysis Experiments

De-ionized water (from 291 to 297 mL) containing reactant powder was placed in a 600-mL beaker. The propeller was centered and lowered into the beaker and the stirrer was adjusted to 1000 rpm. The high mixing speed was required to minimize CL-20 particles flotation. Next, 3 to 9 mL of concentrated NaOH solution of appropriate molarity was introduced into the solution to yield a 300 mL reaction volume.

Samples (2 mL) withdrawn periodically from the reaction were added to test tubes containing appropriate amounts of H_2SO_4, to neutralize the sample. The purposes of neutralization are first to quench the base hydrolysis reaction and secondly to protect the HPLC column from alkaline conditions. The neutralized samples were further diluted with acetonitrile (1:1 by volume) prior to analysis. All samples were analyzed immediately at the end of each run.

RESULTS AND DISCUSSION

A series of kinetic runs for the homogeneous CL-20 alkaline hydrolysis were carried out with initial CL-20 concentrations of about 3 mg/L (~6.849×10^{-6} M) and NaOH concentrations ranging from 0.25 to 10 mM. The experiments were performed at 15, 20, 30, and 40°C. Data for the CL-20 homogeneous alkaline hydrolysis are presented in figure 1. In these studies, the molar ratio of NaOH to CL-20 ranged from 36.5:1 to 1460:1. To validate the assumption that base concentration in the solution was measured at the end of the experiments (when CL-20 is depleted). At the lowest NaOH concentration used (0.25 mM at 40°C), the NaOH consumption was found to be negligible (about 2%); which supports the pseudo-first order kinetics assumption under the present experimental conditions.

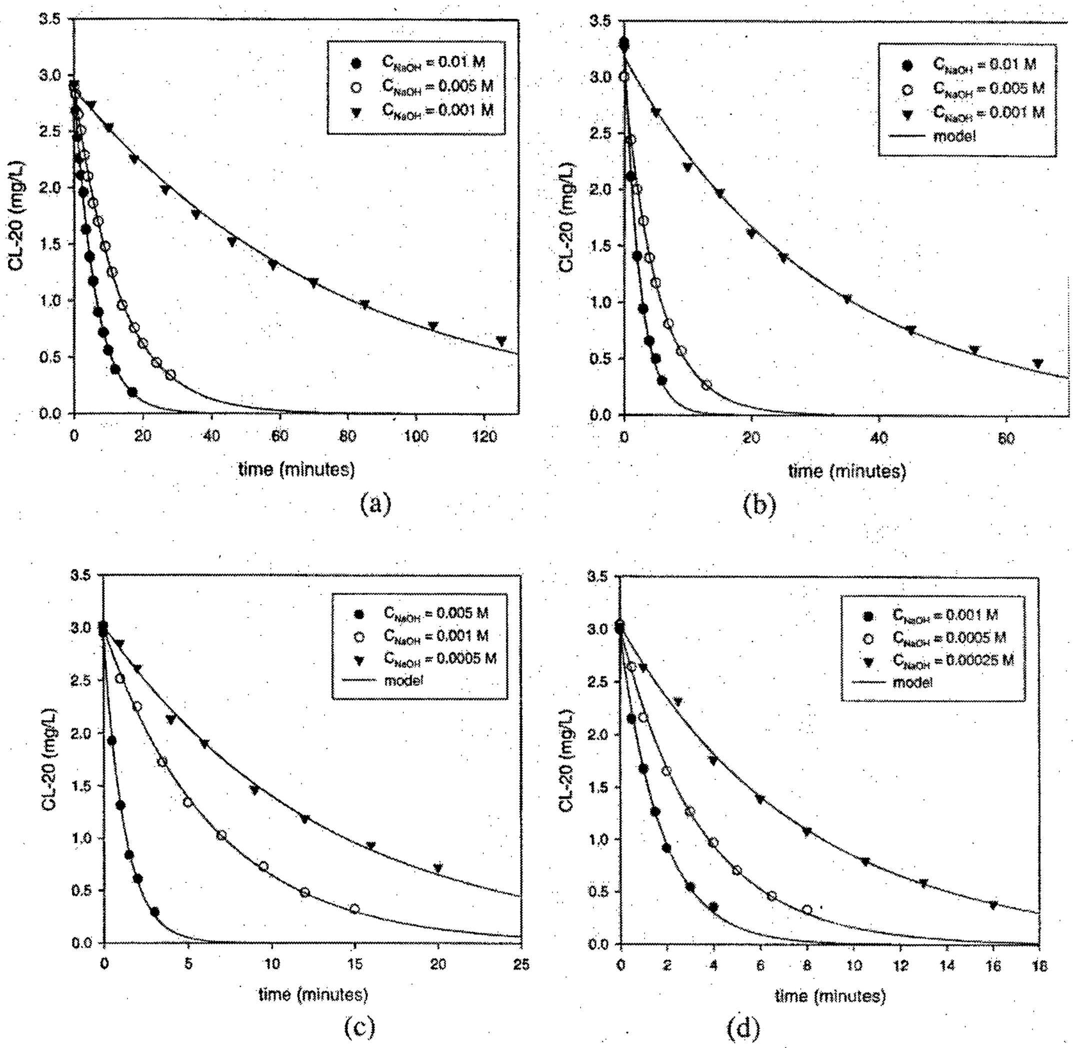


Figure 1
Concentration-time profiles of CL-20 homogeneous alkaline hydrolysis at (a) 15°C, (b) 20°C, (c) 30°C, and (d) 40°C at various alkalinities

Another set of experiments was conducted to examine the kinetics of heterogeneous CL-20 alkaline hydrolysis, with initial CL-20 concentrations at about 500 mg/L (~1.142 x 10^{-3} M) at 15, 20, 30, and 40°. The obtained data are shown in figure 2. In these experiments, the NaOH concentration was varied from 25 to 300 mM, with molar ratios of NaOH to CL-20 ranging from 21.9:1 to 262.8:1. At the lowest NaOH concentration studied (25 mM at 40°C) the decrease in NaOH concentration during heterogeneous alkaline hydrolysis was about 9% and was considered to be within acceptable limits for the application of the pseudo-first order kinetics assumption.

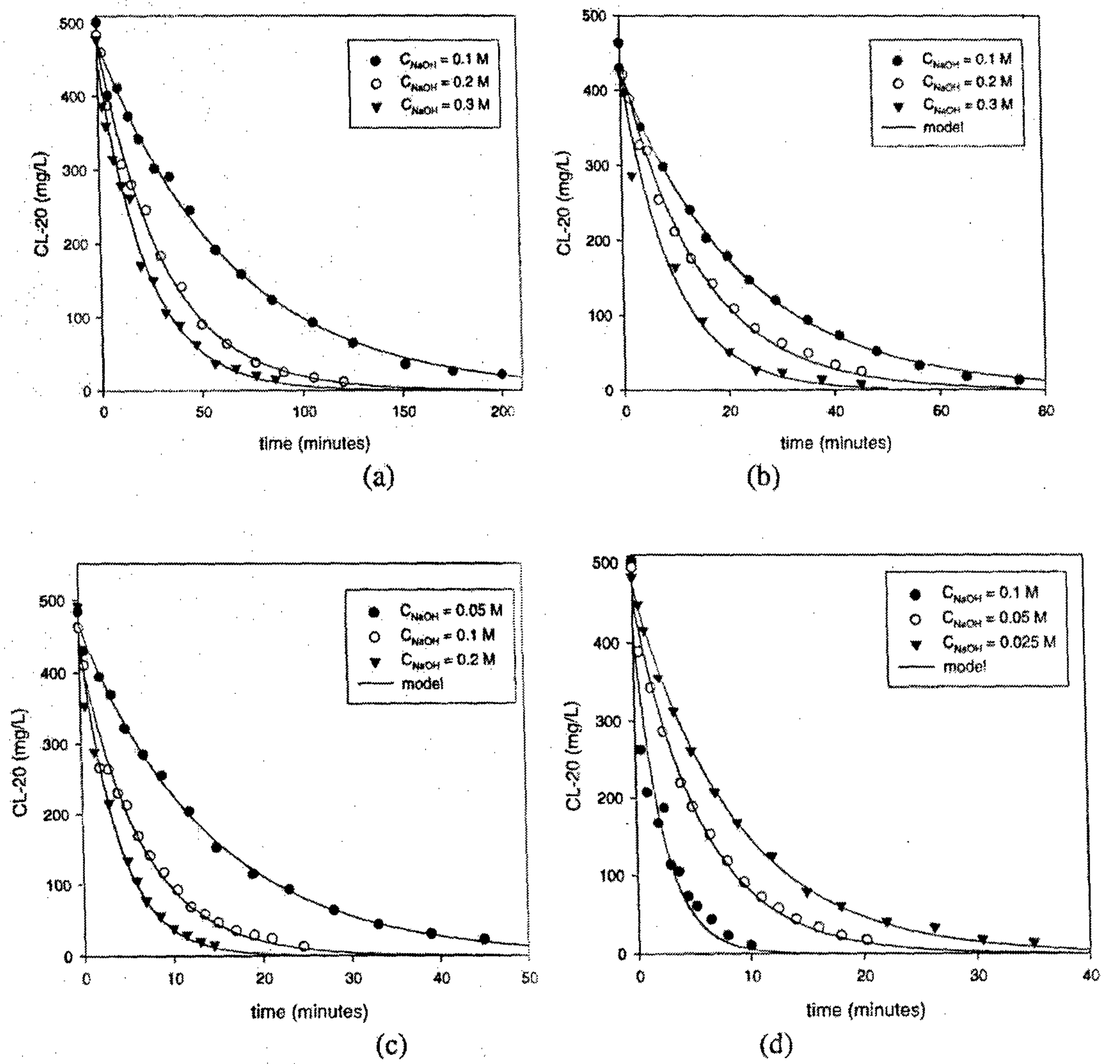


Figure 2
Concentration-time profiles of CL-20 heterogeneous alkaline hydrolysis at (a) 15°C, (b) 20°C, (c) 30°C, and (d) 40°C at various alkalinities

From the concentration-time profiles (figs. 1 and 2) it is clear that the rate of alkaline hydrolysis of CL-20 depends on alkali strength. For example, at 20°C and 3 mg/L of initial CL-20, 85% of the compound, reacts with 10 mM NaOH within 5 min; however, with 1 mM NaOH, it requires about 65 min to achieve the same degree of transformation. The temperature effect on the rate of alkaline hydrolysis of CL-20 is also illustrated in figure 1. For instance at 1 mM NaOH and 3 mg/L of initial CL-20, when the temperature is increased form 20°C to 30°C, the time required for the same extent of removal (85%) drops from 65 to 12 min.

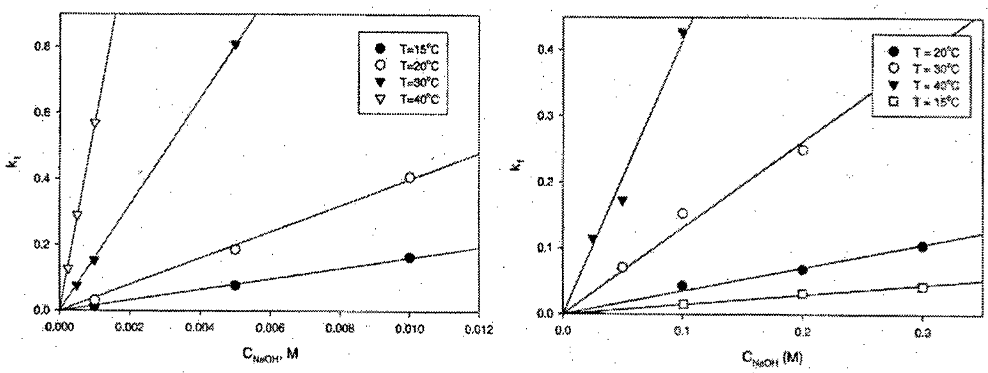
The CL-20 concentration-time profiles were used to obtain the relevant kinetic parameters for homogeneous and heterogeneous alkaline hydrolysis, by applying non-linear regression analysis. The computed pseudo-first order rate constants (k_1) and corresponding standard errors are presented in table 1. The experimental data correlate closely with the assumed pseudo-first order kinetic model with excellent correlation coefficients.

Table 1
Pseudo first-order rate constants k_1 (min^{-1}) and corresponding correlation coefficients (R^2) for alkaline hydrolysis of CL-20 for different NaOH concentrations and temperatures

C_{NaOH}(mM)	15°C	20°C	30°C	40°C
Homogeneous alkaline hydrolysis				
10	0.1639 (0.0025)[a] $R^2 = 0.9987$	0.4086 (0.0103) $R^2 = 0.9982$		
5	0.0776 (0.0007) $R^2 = 0.9994$	0.1869 (0.0025) $R^2 = 0.9993$	0.8089 (0.0160) $R^2 = 0.9991$	
1	0.0129 (0.0003) $R^2 = 0.9961$	0.0320 (0.0009) $R^2 = 0.9962$	0.1531 (0.0030) $R^2 = 0.9986$	0.5696 (0.0155) $R^2 = 0.9979$
0.5			0.0763 (0.0022) $R^2 = 0.9963$	0.2902 (0.0064) $R^2 = 0.9982$
0.25				0.1273 (0.0032) $R^2 = 0.9975$
Heterogeneous alkaline hydrolysis				
300	0.0427 (0.0020) $R^2 = 0.9898$	0.1051 (0.0115) $R^2 = 0.9750$		
200	0.0319 (0.0012) $R^2 = 0.9945$	0.0686 (0.0021) $R^2 = 0.9952$	0.2501 (0.0155) $R^2 = 0.9853$	
100	0.0156 (0.0006) $R^2 = 0.9928$	0.0437 (0.0005) $R^2 = 0.9991$	0.1531 (0.0070) $R^2 = 0.9860$	0.4281 (0.0643) $R^2 = 0.9027$
50			0.0709 (0.0017) $R^2 = 0.9972$	0.1731 (0.0068) $R^2 = 0.9915$
25				0.1151 (0.0019) $R^2 = 0.9988$

[a]Numbers in parentheses are standard errors.

The k_2 values were obtained as the slopes of the plots k_1 versus NaOH concentration (fig. 3). The second-order rate constants obtained at homogeneous conditions (k_2^{hom}) and at heterogeneous conditions (k_2^{het}), by linear regression for the temperatures studied and the corresponding correlation coefficients are presented in table 2. The values of k_2^{hom} are significantly higher than those obtained for k_2^{het}, with ratios of 109, 112, 122, and 137 at temperatures of 15, 20, 30, and 40°C, respectively. The lower k_2^{het} values may be attributed to mass transfer limitations that commonly occur in heterogeneous reactions, which indicate that the heterogeneous hydrolysis of CL-20 may not be under kinetic control.



(a) (b)

The second-order rate constants (k_2) are calculated from the slopes of the curves.

Figure 3
Linear regression analysis using equation 3 for (a) homogeneous and (b) heterogeneous alkaline hydrolysis of CL-20

Table 2
Second-order rate constants (k_2) and corresponding correlation coefficients (R^2)

Temperature (°C)	K_2^{hom} ($M^{-1}min^{-1}$)	K_2^{het} ($M^{-1}min^{-1}$)
15	16.1897	0.1481
	$R^2 = 0.9977$	$R^2 = 0.9769$
20	10.0992	0.3544
	$R^2 = 0.9957$	$R^2 = 0.9607$
30	161.3619	1.3119
	$R^2 = 0.9997$	$R^2 = 0.9591$
40	568.7810	4.1404
	$R^2 = 0.9974$	$R^2 = 0.9733$

The temperature dependency of k_2 can be represented by the Arrhenius law

$$k_2 = Ae^{-\frac{E}{RT}} \tag{5}$$

where A is the frequency factor or Arrhenius constant, E the activation energy (kJ/mol) of the reaction, R the gas constant (8.314 $J.mol^{-1}.{}^{0}K^{-1}$) and T (°K) the absolute temperature. This expression fits the experimental data well over wide temperature ranges and is strongly suggested from various standpoints as being a very good approximation to the true temperature dependency (ref. 3). The parameters, A and E, are determined from a linear least square fit of the logarithm of the obtained average second-order rate constants (table 2) against the reciprocal of the absolute temperature as shown in figure 4. The value of the activation energy, E was calculated as 105.64 KJ/mol for homogeneous alkaline hydrolysis (R^2=0.9979). The apparent activation energy for the heterogeneous reaction was calculated as 98.81 KJ/mol (R^2=0.9970). Although small, this difference in activation energy values could be attributed to external mass-transfer limitations that might not have been fully addressed by the mixing speed used in the heterogeneous experiments. The activation energy values obtained for the CL-20 base hydrolysis are within close range of those reported by Heilmann et al. (refs. 1 and 4) for RDX (99.9 kJ/mol) and HMX (111.9 kJ/mol) and the heterogeneous activation energy reported by Christodoulatos et al. (ref. 5) for nitrocellulose (100.9 kJ/mol). The Arrhenius pre-exponential constants for the homogeneous and heterogeneous reactions are 2.52×10^{20} and 1.34×10^{17}, respectively.

CONCLUSIONS

Alkaline hydrolysis is a simple and effective treatment technology for energetic materials including CL-20. The alkaline hydrolysis of CL-20 above and below solubility limits follows second order kinetics. Homogeneous alkaline hydrolysis rates of CL-20 are higher than heterogeneous rates, and in both cases the reaction is faster in comparison to the alkaline hydrolysis of RDX. The activation energy for CL-20 undergoing alkaline hydrolysis is within close range of the reported activation energies for other nitrated energetic compounds. Further studies are necessary to evaluate mass transfer effects on the alkaline hydrolysis rates of CL-20 and to identify the intermediate and end products of the alkaline reactions.

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